I. RESTRICTED ROTATION IN N,N'-DIMETHYL-N,N'-DIARYLSULFONYLDIAMINOMESITYLENES

II. ATTEMPTED RESOLUTION OF CARBODIIMIDES

BY

MORTON ROTHSTEIN

B.A., University of British Columbia, 1946
M.S., University of Illinois, 1947

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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IN THE GRADUATE COLLEGE OF THE
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I. RESTRICTED ROTATION IN N,N′-DIMETHYL-N,N′-DIARYLSULFONYLDIAMINOMESITYLENES

Introduction

Restricted rotation about the two carbon-nitrogen single bonds in diaminomesitylene has been proved to exist by the isolation of certain *cis*- and *trans*- N,N′-disubstituted-N,N′-dibenzenesulfonyldiaminomesitylenes (1). This investigation was undertaken to establish that restricted rotation exists in N,N′-dimethyl-N,N′-diarylsulfonyldiaminomesitylenes, and to determine whether the reactions of the methyl substituted compounds were analogous to those of the ethyl series.

Discussion Of Results

Diaminomesitylene was treated with one and two moles of methyl iodide, and yielded N-methyl- and N,N′-dimethyldiaminomesitylene respectively. Treatment of the latter with benzenesulfonyl chloride in pyridine yielded *cis*- and *trans*-N,N′-dimethyl-N,N′-dibenzenesulfonyldiaminomesitylene. No methyl group was lost as in the analogous case when N,N′-diethyldiaminomesitylene, under similar conditions, yielded N-ethyl-N,N′-dibenzenesulfonyldiaminomesitylene (1).

N,N′-Dibenzenesulfonyldiaminomesitylene was treated with methyl iodide in alkaline medium, and also yielded *cis*- and *trans*-N,N′-dimethyl-N,N′-dibenzenesulfonyldiaminomesitylene. Methylation of N-methyl-N,N′-dibenzenesulfonyldiaminomesitylene in alkaline medium provided a third method of obtaining the *cis*- and *trans*-N,N′-dimethyl compounds. The N-methyl-N,N′-dibenzenesulfonyldiaminomesitylene was prepared in poor yield both by benzenesulfonation of N-methyldiaminomesitylene, and by limited methylation of N,N′-dibenzenesulfonyldiaminomesitylene. Some dimethylation occurred in the latter reaction, resulting in the formation of the N,N′-dimethyl *cis* and *trans* isomers.

N,N′-Di-*p*-bromobenzene,- di-*p*-toluene- and di-*p*-nitrobenzenesulfonyldiaminomesitylene were prepared by treatment of N,N′-dimethyldiaminomesitylene with the proper sulfonyl chloride in pyridine. The *p*-nitro derivative could not be completely purified because of oily by-products; the *p*-toluene reaction yielded a large amount of monosubstituted product which after isolation and further treatment with *p*-toluenesulfonyl chloride, gave the desired N,N′-di-*p*-toluenesulfonyldiaminomesitylene. Treatment of the diarylsulfonyldiaminomesitylenes with methyl iodide in alkaline medium yielded in each case, *cis* and *trans* isomers.

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II. ATTEMPTED RESOLUTION OF CARBODIIMIDES

Introduction

The resolution of allene type compounds into optical antipodes (1,2) as predicted by Van't Hoff (3) in 1895, showed that the double bonds of the allene carbon atom were non-planar, and thus the groups attached to the terminal carbon atom were also non-planar, causing asymmetry in the molecule. Since carbodiimides have the essential allene bond system, optical activity should exist in these compounds, providing the terminal nitrogen atoms maintain a fixed tetrahedral structure. It was the purpose of this investigation to attempt the resolution of suitable carbodiimides.

Discussion Of Results

Di-(4-dimethylaminophenyl)-carbodiimide was prepared in good yield by the method of Zetzsche (4), desulfurization of the corresponding thiourea taking place in refluxing acetone

with very finely divided lead oxide, using a little sulfur as a catalyst. The di-*d*-camphorsulfonate proved to be unstable and resolution was not attempted.

Di-*α*-pyridylthiourea was desulfurized with lead oxide in xylene at 128°, a 12% yield of di-*α*-pyridylcarbodiimide being obtained. The di-*d*-camphorsulphonate was prepared in ethyl acetate, but no resolution could be effected either from ethyl acetate-ethanol or benzene-ethanol mixtures. The salt tended to decompose if left in solution for long periods of time. Attempted preparation of the mono-*d*-camphorsulfonate yielded two differently rotating salts, $[\alpha]^{25}$ D + 88° and $[\alpha]^{25}$ D + 72° respectively, after recrystallization of the crude material from dry benzene. Analyses did not agree with those for the mono-*d*-camphorsulfonate of di-*α*-pyridylcarbodiimide. Decomposition of either salt with sodium hydroxide gave good recovery of optically inactive di-*α*-pyridylcarbodiimide.

The desulfurization of di-(3-methyl-*α*-pyridyl)-thiourea by either the conditions used for preparing di-(4-dimethylaminophenyl)-carbodiimide or di-*α*-pyridylcarbodiimide was unsuccessful.

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VITA

The author was born on September 8, 1922, in Vancouver, British Columbia, where he obtained his elementary and secondary education. He graduated from King Edward High School in June, 1942, and entered the University of British Columbia in the fall of that year, receiving the degree of Bachelor of Arts with Honors in Chemistry in June, 1946. He held a teaching assistantship in the special Spring Session of 1946. From September, 1946 to July, 1949, he attended the University of Illinois, receiving the degree of Master of Science in June, 1947.

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